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I, TERESA KOLODZIEJCZYK, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2002950860 for a patent by BERTSHELL PTY LTD and MACQUARIE VETERINARY SUPPLIES PTY LTD as filed on 19 August 2002.

WITNESS my hand this
Seventeenth day of April 2003

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ORIGINAL

AUSTRALIA

Patents Act 1990

PROVISIONAL SPECIFICATION FOR THE INVENTION ENTITLED:

Process and Apparatus for Use in Preparing an Aqueous Magnesium Bicarbonate Solution

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This invention is best described in the following statement:

PROCESS AND APPARATUS FOR USE IN PREPARING AN AQUEOUS MAGNESIUM BICARBONATE SOLUTION

Technical Field

The present invention relates to the preparation of an aqueous magnesium bicarbonate solution. More particularly, the invention relates to processes and apparatus for use in the production of an aqueous magnesium bicarbonate solution suitable for oral ingestion,

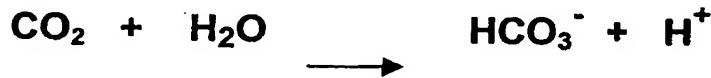
Background of the Invention

The consumption or administration of sodium and potassium bicarbonates has been correlated to the neutralisation of acid in the human body. Amongst other effects, 10 the neutralisation of acid with bicarbonates (potassium bicarbonate in particular) decreases bone resorption, increases the rate of bone formation and stops the decline in muscle and tissue wasting that occurs with ageing and degenerative diseases (see Sebastian et al, 1994 N Eng J Med 330 (25): 1776-81 and Frassetto et al 1997 J Clin Endocrin Metab 82 (1): 254-259).

15 However, both sodium and potassium bicarbonates are known to be toxic to some people at moderate to high dosage rates when consumed for a prolonged period. Thus, there is a need for a bicarbonate in a safe form.

20 There is also a need for a bicarbonate suitable for the prevention and treatment of diseases, in humans and other mammals, where the diseases have high carbon dioxide concentrations and/or high acid concentrations in the disease pathogenesis.

In Patent Application PCT/AU/98/00168 and in Australia Patent No 735 435, a process for the manufacture of a mildly alkaline magnesium bicarbonate solution from a basic magnesium carbonate powder dispersed in water, using carbon dioxide absorbed into the water from the gaseous state, is described. In that process, dissolved carbon 25 dioxide reacts with the magnesium carbonate either while it is still in its solid form as a suspension in water or upon dissolution thereof in water, to form magnesium bicarbonate:



The time required for the above chemical reactions to run to completion to ensure the clarity or clearness of the final solution was stated in Patent Application

PCT/AU/98/00168 and in Australia Patent No 735435 to be not less than 6 hours, typically from 6 hours to seven days, more typically from 24 hours to 72 hours.

It has been found by the applicant to be undesirable to bottle magnesium bicarbonate for oral administration, manufactured from magnesium carbonate by the dissolution thereof with carbon dioxide before it has been stabilised.

On the one hand, it is desirable for the solution to be clear. Because any undissolved magnesium carbonate does not dissolve easily after the solution has been bottled, it is desirable to dissolve all magnesium carbonate powder before bottling the solution, or to bottle the solution when there is no more than a slight haze visible in it, particularly when the pH of the solution is not close to or at the maximum of the aforementioned range of 7.5 to 8.9.

On the other hand, it is desirable for the magnesium bicarbonate solution to have a pH higher than the physiological pH of a mammal, preferably as high as possible within the aforesaid range of 7.5 to 8.9, consistent with the objective of maintaining a clear solution, without the higher pH causing magnesium carbonate to be either precipitated from the solution or not being dissolved or converted into magnesium bicarbonate in the first place.

There accordingly exists a need for a process for the manufacture of a magnesium bicarbonate containing solution that has a decreased reaction time under temperature conditions which are favourable for the rapid dissolution of carbon dioxide in water, without the solution having a pH which is too low.

There also exists a need for a process for the bottling of a magnesium bicarbonate containing solution that will be substantially clear or that will become substantially clear within a relatively short period after bottling, which period may be from one to eight hours after bottling.

Object of the Invention

It is an object of the present invention to overcome or substantially ameliorate at least one of the above disadvantages.

Summary of the Invention

According to a first aspect of the present invention, there is provided a method of preparing a substantially clear aqueous solution containing magnesium bicarbonate, including the steps of:

- contacting, with species resulting from the dissolution of carbon dioxide in water, an aqueous suspension of magnesium carbonate, at suitable conditions of pressure and temperature, so as to obtain an aqueous solution of magnesium bicarbonate; and
- controlling the pH of the said solution so that, after reaction of the said species with the magnesium carbonate, the final pH falls within a range of from about 8,0 to about 8,8.

According to a second aspect of the present invention, there is provided a method of preparing a substantially clear aqueous solution containing magnesium bicarbonate, including the step of contacting, with species resulting from the dissolution of carbon dioxide in water, an aqueous suspension of magnesium carbonate, at suitable conditions of pressure and temperature, so as to obtain an aqueous solution of magnesium bicarbonate and magnesium carbonate, said aqueous solution having a pH, after reaction of the said species with the magnesium carbonate, within a range of from about 8,0 to about 8,8.

The process according to the second aspect of the invention may conveniently therefore also include a step in which the pH is controlled.

The pH may be controlled by decreasing or increasing the pH of the aqueous suspension of magnesium carbonate and of the resulting solution by dissolving in the suspension a larger or a smaller amount of carbon dioxide. Alternatively, the pH may be controlled by increasing or decreasing the amount of magnesium carbonate introduced into the suspension. As another alternative, the pH may be controlled by introducing into the solution protons or a substance which has an effect on the pH.

According to a third aspect of the present invention, there is provided a method of preparing a substantially clear aqueous solution containing magnesium bicarbonate, including the steps of:

- contacting, with species resulting from the dissolution of carbon dioxide in water, an aqueous suspension of magnesium carbonate, at suitable conditions of pressure and temperature, so as to obtain an aqueous solution of magnesium bicarbonate at a pH, after reaction of the said species with the magnesium carbonate, falling within a range of from about 8,0 to about 8,8; and
- agitating the suspension so as to keep in suspension a major portion of the magnesium carbonate until substantially all of the said magnesium carbonate has been converted to dissolved magnesium bicarbonate.

The major portion of the magnesium carbonate may be any proportion from about 30% to about 100% of the magnesium carbonate forming part of the said suspension.

The method according to the second aspect of the invention may conveniently also include a step in which the pH is controlled. This may be achieved by either decreasing or increasing the pH of the aqueous suspension of magnesium carbonate and of the resulting solution by dissolving in the suspension a larger or a smaller amount of carbon dioxide.

Alternatively, the pH may be controlled by increasing or decreasing the amount of magnesium carbonate introduced into the suspension. As another alternative, the pH may be controlled by introducing into the solution protons or a substance which has an effect on the pH.

The pH of the aqueous suspension of magnesium carbonate may advantageously be controlled to be above about 8, ideally between about 8,2 and about 8,8.

The method according to these aspects of the invention may include the step of controlling the pressure at an absolute pressure of from about 50 kPa to about 500 kPa.

The aqueous suspension of magnesium carbonate preferably contains from about 50 mg to about 200 milligrams of magnesium per litre of water, more particularly from about 90 mg per litre to 150 mg per litre, even more particularly from about 100 mg per litre to about 140 mg per litre. The aqueous solution of magnesium bicarbonate obtained may have a concentration of bicarbonate anions from about 200 mg per litre to about 1000 mg per litre, more particularly from about 400 mg per litre to 800 mg per litre, even more particularly from about 500 mg per litre to 700 mg per litre.

By carefully following the teachings of the present invention, the aqueous solution of magnesium bicarbonate may be produced in commercial quantities in less than about 6 hours.

The species resulting from the dissolution of carbon dioxide in water may include protons and bicarbonate ions. Alternatively or additionally, it may include carbonic acid.

The magnesium carbonate is preferably contacted with a stoichiometric quantity of species resulting from the dissolution of carbon dioxide in water, or with a quantity of such species which exceeds a stoichiometric quantity by from about 0% to about 20%, preferably by no more than about 10%, more preferably, by no more than about 1% to about 5%.

The temperature of the aqueous suspension of magnesium carbonate may also be controlled. The temperature may be controlled between about 0°C and about 25°C.

It is to be understood that at lower temperatures, the rate of dissolution of carbon dioxide in water is faster than at higher temperatures. However, the rate of the reaction of magnesium carbonate with the species resulting from the dissolution of carbon dioxide in water, to form magnesium bicarbonate, is lower at lower temperature. Thus, the 5 temperature of the aqueous suspension of magnesium carbonate water may be controlled at such a level as to achieve a desired absorption of carbon dioxide into the suspension consistent with a desired rate of reaction between magnesium carbonate and the species formed as a result of the dissolution of carbon dioxide in the suspension. Preferably, the temperature is maintained below about 25°C in the range between about 1°C and about 10 20°C, more preferably below about 18°C in the range between about 5°C and about 18°C, even more preferably in the range between about 10°C and about 18°C, ideally in the range of from about 12°C to about 18°C, even more ideally between about 12°C and about 15°C.

The contacting step of either the first or the second aspect of the invention may be 15 conducted either continuously or batchwise.

The method in accordance with the first and second aspects of the invention may conveniently also include the additional step of bottling the said aqueous solution of magnesium bicarbonate, preferably under an atmosphere containing carbon dioxide, preferably at an absolute pressure of from about 50 kPa to about 500 kPa. Alternatively, 20 the solution may be bottled under air or nitrogen, at a pressure from about 50kPa to about 500kPa.

The bottling step is preferably carried out when the magnesium bicarbonate solution is clear, or, in order to reduce processing time, whilst the turbidity of the magnesium bicarbonate solution is no more than a slight haze and the pH falls within the range of 25 about pH 7.0 to pH 9.0, ideally from about pH 7.8 to pH 8.8, more ideally from about pH 8.0 to pH 8.6. It has been found that if the turbidity is low enough, the solution will clear up after bottling if the pH falls within this range, but when the turbidity is too high, the solution either does not clear up after bottling or the end pH, after complete reaction of said species with the magnesium carbonate, is too high. If the pH value exceeds pH 9.0, 30 the taste of the magnesium bicarbonate solution becomes unacceptable as it tends to be too caustic. Above pH 9.0 carbonate floccules may reappear in the solution. If the pH value falls below pH 7.0, the medical value of the magnesium bicarbonate solution is largely negated.

In order to prevent the presence of unwanted foreign matter in the magnesium bicarbonate solution, the method according to the first, second and third aspects of the invention may include the step of passing any one or more of the suspension, the solution and the water to be used for the preparation of the aqueous magnesium carbonate suspension through a filter having a maximum pore size of about 10 microns, preferably having a maximum pore size of about 5 microns, more preferably having a maximum pore size of about 2 microns.

According to a fourth aspect of the present invention, there is provided an apparatus suitable for preparing an aqueous solution of magnesium bicarbonate, comprising:

- 10 - means for contacting, with species resulting from the dissolution of carbon dioxide in water, a suspension of powdered magnesium carbonate in water so as to form an aqueous solution of magnesium bicarbonate; and
- means for controlling the pH of the solution between about 7 and about 9 by adjusting the amount of at least one of the said species and the said powdered magnesium carbonate that is contacted with the other.

The apparatus according to the third aspect of the invention may also comprise means for keeping in suspension a major portion of said powdered magnesium carbonate.

According to a fifth aspect of the present invention, there is provided an apparatus suitable for preparing an aqueous solution of magnesium bicarbonate, comprising:

- 20 - means for contacting, with species resulting from the dissolution of carbon dioxide in water, a suspension of powdered magnesium carbonate in water so as to form an aqueous solution of magnesium bicarbonate; and
- means for keeping in suspension a major portion of said powdered magnesium carbonate until substantially all of the suspended magnesium carbonate has been converted to dissolved magnesium bicarbonate.

The apparatus according to the fifth aspect of the invention may also comprise means for controlling the pH of the solution between about 7 and about 9. This may be achieved by means adapted to adjust the amount of at least one of the said species and the said powdered magnesium carbonate that is present in the apparatus.

- 30 The apparatus according to the fourth and fifth aspects of the invention may also comprise means for bottling the solution of magnesium bicarbonate.

The means for contacting may comprise means, such as a tank of sufficient size, for containing the suspension and the species resulting from the dissolution of carbon dioxide in water. In a batch process, a tank large enough to contain all of the magnesium

bicarbonate solution required for a production run in which a certain number of bottles are filled with the solution, may be provided. In the case of a continuous process, a smaller container may be sufficient for the contacting step, although a suitable reactor and/or clarifier or other similar but suitable pieces of equipment may be provided to
5 ensure that the reaction between the magnesium carbonate and the said species is permitted to run to substantial completion.

The means for contacting with magnesium carbonate the species resulting from the dissolution of carbon dioxide in water may also comprise means for dissolving carbon dioxide in the water or in the said suspension so as to form a solution containing the said
10 species.

The means for dissolving carbon dioxide may comprise a sparger comprising a fine mesh such as a stocking like mesh, or another suitable device capable of breaking up the carbon dioxide into small bubbles. The sparger may conveniently comprise a porous separation means adapted to separate pressurised carbon dioxide from water into which
15 the carbon dioxide is to be dissolved, the pores of the separation means extending from a gas side thereof to a water side thereof, in use, and to break the carbon dioxide up into a plurality of small bubbles, for increasing the intimacy of contact between the carbon dioxide and the water.

The means for dissolving carbon dioxide may comprise, in addition to or as an
20 alternative to the aforementioned sparger means, a tube and a helical baffle locatable within the tube, means for disposing the tube in a substantially vertical position, means for introducing carbon dioxide into a first end of the tube which, in use, is located below a second end of the tube, and means for introducing water or the said aqueous suspension of magnesium carbonate at either of the first end or the second end thereof, whereby
25 carbon dioxide is allowed to bubble through the tube and to be intimately contacted with the water or said aqueous suspension of magnesium carbonate.

The apparatus may further comprise means for bottling the magnesium bicarbonate solution. The means may be or may comprise means for bottling the solution with air, nitrogen or carbon dioxide under a pressure from about 120kPa to about 500kPa.

30 According to a sixth aspect of the present invention, there is provided a method of preparing a substantially clear aqueous solution containing magnesium bicarbonate, including the steps of:

- contacting, with species resulting from the dissolution of carbon dioxide in water, an aqueous suspension of magnesium carbonate, at suitable conditions of pressure

and temperature, so as to obtain an aqueous solution of magnesium bicarbonate at a pH, after reaction of the said species with the magnesium carbonate, falling within a range of from about 8,0 to about 8,8;

- controlling the pH of the said solution within the said range until substantially all of the said magnesium carbonate has been converted to dissolved magnesium bicarbonate; and
- bottling the said magnesium bicarbonate solution.

According to a seventh aspect of the present invention, there is provided a method of preparing a substantially clear aqueous solution containing magnesium bicarbonate, including the steps of:

- contacting, with species resulting from the dissolution of carbon dioxide in water, an aqueous suspension of magnesium carbonate, at suitable conditions of pressure and temperature, so as to obtain an aqueous solution of magnesium bicarbonate at a pH, after reaction of the said species with the magnesium carbonate, falling within a range of from about 8,0 to about 8,8;
- agitating the suspension so as to keep in suspension a major portion of the magnesium carbonate until substantially all of the said magnesium carbonate has been converted to dissolved magnesium bicarbonate; and
- bottling the said aqueous magnesium bicarbonate solution.

According to an eighth aspect of the present invention, there is provided an apparatus suitable for preparing an aqueous solution of magnesium bicarbonate, comprising:

- means for contacting, with species resulting from the dissolution of carbon dioxide in water, a suspension of powdered magnesium carbonate in water so as to form an aqueous solution of magnesium bicarbonate;
- means for controlling the pH of the solution between about 7 and about 9 by adjusting the amount of at least one of the said species and the said powdered magnesium carbonate that is contacted with the other; and
- means for bottling the said solution of magnesium bicarbonate.

According to a ninth aspect of the present invention, there is provided an apparatus suitable for preparing an aqueous solution of magnesium bicarbonate, comprising:

- means for contacting, with species resulting from the dissolution of carbon dioxide in water, a suspension of powdered magnesium carbonate in water so as to form an aqueous solution of magnesium bicarbonate;

- means for keeping in suspension a major portion of said powdered magnesium carbonate until substantially all of the suspended magnesium carbonate has been converted to dissolved magnesium bicarbonate; and
- means for bottling said solution of magnesium bicarbonate.

5 According to a tenth aspect of the present invention, there is provided a process for the manufacture of an aqueous solution comprising dissolved magnesium bicarbonate and dissolved magnesium carbonate, wherein the process includes the step of contacting an aqueous suspension of a source of magnesium cations with such an amount of a species resulting from the dissolution of carbon dioxide in water and having an initial pH below
10 about 7 as is sufficient to result in the said aqueous solution comprising dissolved magnesium bicarbonate and dissolved magnesium carbonate having a pH of from about 7.5 to about 8.9 and to be substantially clear.

15 The process according to the tenth aspect of the present invention may include a step in which the aqueous suspension of a source of magnesium cations is prepared. This step may include the suspension of a suitably pulverised or particulate solid compound of magnesium in water.

20 The process according to the tenth aspect of the present invention may also include a step in which the species resulting from the dissolution of carbon dioxide in water is prepared so as to result in a carbonated solution having a pH below 7, preferably well below 7. The pH of the carbonated solution may be controlled by the dissolution of such an amount of carbon dioxide as would result in the desired pH.

The species resulting from the dissolution of carbon dioxide in water may include protons and bicarbonate ions. Alternatively or additionally, it may include carbonic acid.

25 The process may include the step of contacting an aqueous suspension of a source of magnesium cations with carbon dioxide gas and mixing the contacted aqueous suspension. The contacted and mixed suspension may be recontacted with carbon dioxide gas one or more times. In one form of the invention, a flowing aqueous suspension of a source of magnesium cations is contacted with bubbles of carbon dioxide gas and the contacted aqueous suspension is subsequently mixed. In one particular form of the
30 invention, a flowing aqueous suspension of a source of magnesium cations is contacted with bubbles of carbon dioxide gas in a contacting vessel which is linked to a mixing vessel and the contacted aqueous suspension is subsequently transferred to the mixing vessel where it is mixed and then recirculated to the contacting vessel. This process is

repeated until the pH of the aqueous solution is between about 7.5 to 9.0, more usually between 8.0 and 9.0, 8.1 to 8.9 and even more usually between about 8.2 and 8.8 and thereafter the solution is mixed and optionally recirculated (without contacting the solution during the recirculation step with carbon dioxide) until the source of magnum cations has substantially dissolved to form an aqueous solution of magnesium bicarbonate and magnesium carbonate. The solution may be thereafter sterilised and bottled.

According to an eleventh aspect of the present invention, there is provided a process for the manufacture of an aqueous solution comprising dissolved magnesium bicarbonate or dissolved magnesium bicarbonate and dissolved magnesium carbonate, wherein the process includes the step of: (i) contacting an aqueous suspension of a source of magnesium cations with bubbles of carbon dioxide gas, (ii) agitating the contacted aqueous suspension, (iii) recontacting the agitated contacted aqueous suspension with bubbles of carbon dioxide gas, and (iv) repeating steps (i) to (iii) as required, to provide a pH in the aqueous solution of from about 7.5 to about 9.

The invention also extends to the product of the process according to the invention.

The aqueous solution may be substantially clear or may be slightly turbid. Usually a slightly turbid solution will become clear when it is placed in a closed container such as when it is bottled and thereafter allowed to stand.

The aqueous solution comprising dissolved magnesium bicarbonate or dissolved magnesium bicarbonate and dissolved magnesium carbonate preferably contains from about 50 mg to about 200 milligrams of magnesium per litre of water, more particularly from about 90 mg per litre to 150 mg per litre, even more particularly from about 100 mg per litre to about 140 mg per litre.

The aqueous solution comprising dissolved magnesium bicarbonate or dissolved magnesium bicarbonate and dissolved magnesium carbonate may have a concentration of bicarbonate anions from about 200 mg per litre to about 1000 mg per litre, more particularly from about 400 mg per litre to 800 mg per litre, even more particularly from about 500 mg per litre to 700 mg per litre.

The aqueous solution comprising dissolved magnesium bicarbonate or dissolved magnesium bicarbonate and dissolved magnesium carbonate preferably has a pH as high as possible within the range of from 7.5 to 8.9, consistent with the objective of maintaining a clear solution, without the higher pH causing magnesium carbonate

containing species to be either precipitated from the solution or not being dissolved or converted into magnesium bicarbonate in the first place.

It has been found that a variable which influences the solubility of magnesium carbonate containing species is the relative concentrations of carbonate and bicarbonate in the solution, which, in turn, is a function of pH. Thus, the higher the pH, the greater the fraction that will be present in the form of carbonate, and the greater the likelihood, therefore, of magnesium carbonate precipitating or not going into solution.

The pH of the aqueous suspension of magnesium carbonate may advantageously be controlled to be above about 8, ideally between about 8.2 and about 8.6.

This may be achieved by either decreasing or increasing the pH of the aqueous suspension of magnesium carbonate and of the resulting solution by dissolving in the suspension a larger or a smaller amount of carbon dioxide.

Alternatively, the pH may be controlled by increasing or decreasing the amount of magnesium carbonate introduced into the suspension. As another alternative, the pH may be controlled by introducing into the solution a physiologically acceptable acid such as any acid acceptable for use in the food or beverage industries, including tartaric acid, citric acid, phosphoric acid or lactic acid.

The pH may be controlled by decreasing or increasing the pH of the aqueous suspension of magnesium carbonate by adding more or less of the species resulting from the dissolution of carbon dioxide in or by dissolving in the suspension a larger or a smaller amount of carbon dioxide. Alternatively, the pH may be controlled by increasing or decreasing the amount of magnesium carbonate introduced into the suspension. As another alternative, the pH may be controlled by introducing into the solution protons or a substance which has an effect on the pH.

As a source of magnesium cations, any compound of magnesium containing carbonate and/or hydroxide and/or oxide groups, whether or not in combination with other elements or groups of elements, may be used. Compounds of magnesium that may be used include the normal carbonates of magnesium, including magnesite $[MgCO_3]$, magnesium oxide $[MgO]$, barringtonite $[MgCO_3 \cdot 2H_2O]$, nesquehonite $[MgCO_3 \cdot 3H_2O]$ and lansfordite $[MgCO_3 \cdot 5H_2O]$, as well as the basic (or hydroxyl-containing) carbonates of magnesium having the general formula $xMgCO_3 \cdot yMg(OH)_2 \cdot zH_2O$, including artinite $[MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O]$, hydromagnesite $[4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O]$, dypingite $[4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O]$, and an as yet unnamed octahydrate

[$4\text{MgCO}_3\text{Mg(OH)}_2\cdot 8\text{H}_2\text{O}$]. It has been found that the pentahydrate or dypingite form of magnesium carbonate hydroxide works particularly well. It is also commercially available in food grade, which is required for the manufacture of potable solutions of magnesium bicarbonate that meets the strictest health standards.

Commercially, magnesium carbonate is available in two forms, one of which has a bulk density of about 0.4 g/mL whilst the other has a bulk density of about 0.2 to about 0.3 g/mL. The grade with the lower bulk density is preferred because it has been found to be more reactive and to dissolve at a faster rate in the process according to the invention, than the one with the higher bulk density.

It has been found that the degree to which magnesium carbonate is precipitated or prevented from dissolving or from reacting with the species resulting from the dissolution of carbon dioxide in water, is dependent on temperature, but also on the presence of other cations and anions in the aqueous solution, such as calcium ions which tend to combine with magnesium and iron cations in solutions as aforementioned to form various so-called double salts of magnesium carbonate such as huntite [$\text{CaMg}_3(\text{CO}_3)_4$], siderite [FeCO_3], dolomite [$\text{CaMg}(\text{CO}_3)_2$] or calcite [CaCO_3]. If desired, from a physiological perspective, to have calcium and iron cations present in the solution, then any of the aforementioned compounds may also be used as a source of magnesium cations.

The solubilities in water of some of the carbonates of magnesium, expressed as the solubility product K_{sp} , are as follows:

Compound	Solubility / Solubility Product
Magnesite [MgCO_3]	Solubility product*1: 1.0×10^{-5}
$\text{MgCO}_3\cdot\text{H}_2\text{O}$	Solubility product*1: 2.7×10^{-5}
Barringtonite [$\text{MgCO}_3\cdot 2\text{H}_2\text{O}$]	Solubility product*1: 2.3×10^{-5}
Nesquehonite [$\text{MgCO}_3\cdot 3\text{H}_2\text{O}$]	Solubility product*1: 8.9×10^{-6}
Hydromagnesite [$3\text{MgCO}_3\text{Mg(OH)}_2\cdot 3\text{H}_2\text{O}$]	Solubility: .04 g per 100 cc in cold water and .011 g per 100 cc in cold water*2
Dypingite [$4\text{MgCO}_3\text{Mg(OH)}_2\cdot 5\text{H}_2\text{O}$]	Solubility: 1 part in 300 parts water*3

*1 Source: Kirk-Othmer: Encyclopedia of Chemical Technology, Fourth Edition, John Wiley and Sons, 1991, Vol 15, p680;

*2 Handbook of Chemistry and Physics, 55th Edition (1974 to 1975), B-105;

*3 Merck Index

It is sometimes advantageous to prepare a magnesium bicarbonate solution containing calcium cations at a concentration at most equal to and preferably lower than that which would cause insoluble calcium species to either not dissolve or to be precipitated from the solution, thereby allowing the aqueous solution to clarify on standing. Calcium carbonate
5 is less soluble than magnesium carbonate, with the result that calcium cations present in either the water or the magnesium carbonate to contribute to the formation of calcium carbonate (calcite) and/or dolomite and/or other insoluble calcium species, which contribute to cloudiness in the magnesium bicarbonate solution. Because of an equilibrium between carbonate and bicarbonate species in solution, which equilibrium is
10 shifted in favour of carbonate species at increasing pH, the presence in the solution of calcium cations places a restriction on the amount of magnesium bicarbonate that can be maintained in solution within the desired pH range of 8,2 to 8,9. Accordingly, where it is important to maximise the amount of dissolved magnesium bicarbonate that is to be administered to a patient, the concentration of calcium cations in the water and in the
15 magnesium carbonate that are used in the process according to the invention, is thus preferably as low as is practically possible.

In one embodiment of the invention, a source of magnesium carbonate is used which has been selected to have a low concentration of calcium cations. Preferably, the concentration of calcium cations in the source of magnesium carbonate is less than the
20 concentration of calcium cations in the source of magnesium carbonate, for a given water quality, than a concentration of calcium cations that would correspond with the maximum solubility of calcium carbonate in a magnesium bicarbonate and magnesium carbonate solution in the said water, having a temperature falling within the temperature ranges and having a pH approaching the higher end of the pH ranges contemplated by the invention.

25 In another embodiment of the invention, a source of water is used which has been selected to have a low concentration of calcium cations. In this embodiment of the invention, the water may be selected so as to contain less calcium cations than would correspond with the maximum solubility of calcium carbonate in a magnesium bicarbonate and magnesium carbonate solution having a temperature falling within the temperature ranges and having a pH approaching the higher end of the pH ranges contemplated by the invention.

The invention also extends to a process for the manufacture of an aqueous solution comprising dissolved magnesium bicarbonate or dissolved magnesium bicarbonate and

dissolved magnesium carbonate, including a step of reducing the concentration of calcium cations in the solution.

The concentration of calcium cations may be reduced by creating conditions favouring the precipitation of calcium carbonate and by the removal of precipitated calcium carbonate from the solution prior to bottling of the magnesium bicarbonate solution.

The solubility of calcium carbonate (calcite) is stated by the Handbook of Chemistry and Physics, 55th Edition (1974 to 1975), page B-77 as 0,0014 grams per 100 cc in water at a temperature of 25°C and 0,0018 grams per 100 cc in hot water (at a temperature of 10 75°C). This equates to 14 and 18 mg per litre respectively. According to the same source, the solubility of magnesium carbonate (as the pentahydrate) is 0,176 g per 100 cc in cold water (1760 mg per litre), whilst the solubility of dolomite is 0,032 g per 100 cc in water at a temperature of 18°C (32 mg per litre).

Thus, it is advantageous that the concentration of calcium compounds or ions in the 15 water and any other ingredients used to prepare the aqueous solution is about equal to or lower than that whereby insoluble calcium species would result, thereby allowing a substantially clear aqueous solution to be prepared. The above solubility figures provide guidance as to the upper concentration levels of calcium ions that can be tolerated in the aqueous solution.

20 One way of removing calcium ions from the water used to prepared the aqueous solution, is by the distillation of the water.

Another way is by the use of reverse osmosis through a suitable membrane.

An alternative way to remove calcium ions is by means of ion exchange. Cation exchange may be done by replacing calcium ions with alkali metal cations or with 25 protons.

Still another way is through the precipitation and removal, in a separate step, of calcium- species. Thus, by taking advantage of the differences in-solubilities of magnesium and calcium carbonates, by creating conditions in the solution which favour the presence of carbonate over the presence of bicarbonate and by accurately controlling the pH, it is possible to precipitate calcium carbonate in preference over magnesium carbonate.

One possibility is to pass the water through a a packed column containing magnesium carbonate.

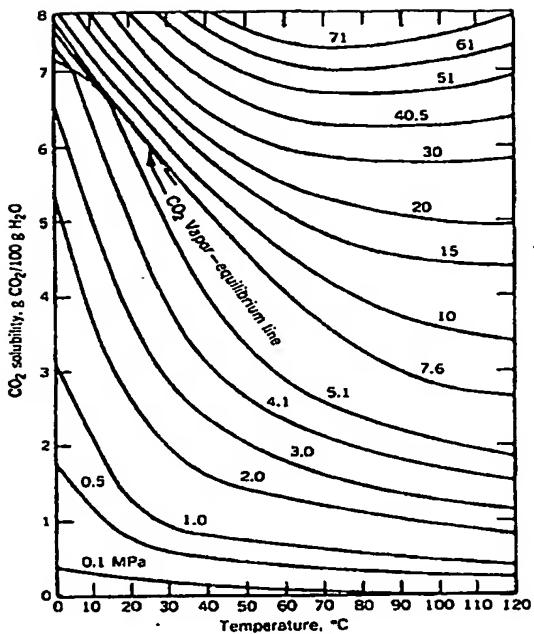
Excess calcium ions may be precipitated from the solution. The precipitate may be separated from the solution by known methods of separation of solids from liquids, such as gravitational settling, filtration, and centrifugation.

The process according to the first aspect of the invention may also include the step of controlling the pressure at an absolute pressure of from about 50 kPa to about 500 kPa. In order to ensure or enhance the dissolution of carbon dioxide and/or to facilitate in the separation of calcium and magnesium, the partial pressure of carbon dioxide may be controlled within a desired range of 1×10^{-12} atmospheres to 50 atmospheres, preferably above 1×10^{-10} atmospheres, more preferably, above 1×10^{-9} atmospheres.

The temperature of the aqueous suspension of magnesium carbonate may also be controlled. The temperature may be controlled between above about 0°C and about 25°C. More specifically, the temperature may be controlled in the range between about 1°C and about 20°C, more preferably below about 18°C, alternatively between about 2°C and about 18°C, between about 2°C and about 18°C, between about 2°C and about 15°C, between about 2°C and about 12°C, between about 2°C and about 10°C, between about 2°C and about 8°C, between about 2°C and about 5°C, alternatively between about 5°C and about 18°C, even more preferably in the range between about 10°C and about 18°C, ideally in the range of from about 12°C to about 18°C., even more ideally between about 12°C and about 15°C, alternatively between about 5°C and about 15°C, between about 5°C and about 12°C, or between about 5°C and about 10°C.

It is to be understood that at lower temperatures, the rate of dissolution of carbon dioxide in water is faster than at higher temperatures. However, the rate of the reaction of magnesium carbonate with the species resulting from the dissolution of carbon dioxide in water, to form magnesium bicarbonate, is lower at lower temperature. Thus, the temperature of the aqueous suspension of magnesium carbonate water may be controlled at such a level as to achieve a desired absorption of carbon dioxide into the suspension consistent with a desired rate of reaction between magnesium carbonate and the species formed as a result of the dissolution of carbon dioxide in the suspension.

The solubility of carbon dioxide in water at various pressures and temperatures is as follows:



Source: Kirk-Othmer: Encyclopedia of Chemical Technology, Fourth Edition, John Wiley and Sons, 1991, Vol 5, p36

5 The contacting step of either the first or the second aspect of the invention may be conducted either continuously or batchwise.

By carefully following the teachings of the present invention, the aqueous solution of magnesium bicarbonate may be produced in commercial quantities in less than about 6 hours.

If required, the process in accordance with the first aspect of the invention may 10 conveniently also include the additional step of bottling the said aqueous solution of magnesium bicarbonate or magnesium bicarbonate and magnesium carbonate, under an atmosphere containing carbon dioxide, preferably at an absolute pressure of from about 50 kPa to about 500 kPa. Alternatively, the solution may be bottled under air or nitrogen, at a pressure from about 50kPa to about 500kPa.

15 The bottling step is preferably carried out when the magnesium bicarbonate solution is clear, or, in order to reduce processing time, whilst the turbidity of the magnesium bicarbonate solution is no more than a slight haze and the pH falls within the range of about pH 7.0 to pH 9.0, ideally from about pH 7.8 to pH 8.8, more ideally from about pH 8.0 to pH 8.8. It has been found that if the turbidity is low enough, the solution will clear 20 up after bottling if the pH falls within this range, but when the turbidity is too high, the solution either does not clear up after bottling or the end pH, after complete reaction of

said species with the magnesium carbonate, is too high. If the pH value exceeds pH 9.0, the taste of the magnesium bicarbonate solution becomes unacceptable as it tends to be too caustic. Above pH 9.0 carbonate floccules may reappear in the solution. If the pH value falls below pH 7.0, the medical value of the magnesium bicarbonate solution is
5 largely negated.

It has been found that by preparing an aqueous solution comprising dissolved magnesium bicarbonate or dissolved magnesium bicarbonate and dissolved magnesium carbonate that contains from about 120 mg per litre to about 140 mg per litre of magnesium ions, that has a pH of about 8.2 to about 8.8, that is substantially saturated
10 with magnesium carbonate and contains so much magnesium bicarbonate as is consistent with the saturated concentration of magnesium carbonate, there is no need for the solution to be bottled with additional carbon dioxide, so that it can be bottled and handled as a "still" product.

In order to prevent the presence of unwanted foreign matter in the solution, the
15 process according to the first aspect of the invention may include the step of passing any one or more of the suspension, the solution and the water to be used for the preparation of the aqueous magnesium carbonate suspension through a filter, conveniently having a maximum pore size of about 10 microns, preferably having a maximum pore size of about 5 microns, more preferably having a maximum pore size of about 2 microns.

If the magnesium bicarbonate solution according to the invention is to be used as a potable drink or for medical purposes, it should contain as few micro-organisms as possible. Ideally, there should not be any micro-organisms present in the solution.
20

The process according to the first aspect of the invention may thus include the additional step of sterilising at least one of and preferably all of the materials and any
25 apparatus used in the manufacture of the solution comprising dissolved magnesium bicarbonate and magnesium carbonate. Sterilisation may be achieved by ozonation and/or by treatment with ultraviolet light.

Sterilisation of feed water or any of the process streams, suspensions or solutions is conveniently applied in steps. In a first step or series of steps, a source of feed water for
30 use in the production of the solution comprising dissolved magnesium bicarbonate and magnesium carbonate may be treated with ozone so as to maintain a substantially constant ozone concentration of at least about 0.4 parts per million, preferably in the range of from about 0.3 to about 0.5 parts per million. In another step, the source of feed water for use

in the production of the solution comprising dissolved magnesium bicarbonate and magnesium carbonate may be treated with ultra violet light. In additional or alternative steps, a suspension of the source of magnesium carbonate or a product solution of dissolved magnesium bicarbonate and magnesium carbonate may be treated with at least 5 one of the ozone and ultraviolet treatments as described above.

The process according to the first aspect of the invention is preferably conducted in a clean environment, which may be managed in accordance with a ruling Clean In Place (CIP) code of practice.

Tests should be done regularly to ascertain whether the magnesium bicarbonate 10 solution is sterile. As an example, a microbiological count should be done before and after UV light treatment and ozonation as described above.

According to a tenth aspect of the present invention, there is provided an apparatus for the manufacture of an aqueous solution comprising dissolved magnesium bicarbonate and dissolved magnesium carbonate, the apparatus comprising means for contacting an 15 aqueous suspension of a source of magnesium cations with such an amount of a species resulting from the dissolution of carbon dioxide in water and having an initial pH below about 7 as is sufficient to result in the said aqueous solution comprising dissolved magnesium bicarbonate and dissolved magnesium carbonate having a pH of from about 7.5 to about 8.9 and to be substantially clear.

20 The apparatus according to the tenth aspect of the invention may conveniently include means for preparing the aqueous suspension of a source of magnesium cations. This means may also include means for keeping in suspension a major portion of said source of magnesium cations.

25 The apparatus according to the tenth aspect of the invention may further include means for preparing the aqueous solution comprising species resulting from the dissolution of carbon dioxide in water.

Conveniently, the apparatus according to the tenth aspect of the invention may include means for controlling the pH of the solution.

30 The apparatus according to the tenth aspect of the invention may also include means for controlling the pressure and/or the temperature of the solution.

The apparatus according to the tenth aspect of the invention may include means for bottling the said aqueous solution of magnesium bicarbonate and magnesium carbonate.

Filter means for removing from any one or more of the suspension, the solution and the water to be used for the preparation of the aqueous magnesium carbonate suspension, may also be provided. Conveniently, the filter has a maximum pore size of about 10 microns. The pore sizes are preferably a maximum of about 5 microns, more preferably a maximum of about 2 microns.

The apparatus according to the second aspect of the invention may further include means for sterilising the apparatus and at least one of and preferably all of the suspensions and solutions processed by the apparatus.

Brief Description of the Drawings

One embodiment of an apparatus in accordance with the second aspect of the present invention will now be described by way of example with reference to the accompanying drawings wherein:

Figure 1 is a diagrammatical flow diagram of one portion of a process in accordance with the first aspect of the invention and an apparatus in accordance with the second aspect of the invention; and

Figure 2 is a diagrammatical flow diagram of another portion of a process in accordance with the first aspect of the invention and an apparatus in accordance with the second aspect of the invention.

Detailed Description of the Drawings

Referring to Figure 1, there is shown a first portion of an apparatus 10 for the manufacture of an aqueous solution comprising dissolved magnesium bicarbonate.

A second portion of the apparatus 10 is shown in Figure 2.

The apparatus 10 comprises a tank T1 for receiving and for treating raw water by means of ultraviolet light. The raw water is transferred into the tank T1 by means of an unloading pump P1. A recirculating pump P2A is provided for recirculating the contents of tank T1 through either one or both of two ultraviolet treatment units UV1 and UV2.

From the tank T1, ultraviolet light treated water is transferred, by means of a transfer pump P2B, via a series of filters F1, F2 and F3, to one of two tanks T2 and T3 for ozone treatment. The filter F1 has a nominal pore size of 1 micron, whilst the filter F2 has a nominal pore size of 0,45 micron and the filter F3 has a nominal pore size of 0,2 micron.

After filtration, the water is passed through an ozone generator O1, in a single pass, so as to achieve an ozone concentration of around 0.2 ppm in the water, before it is discharged into either tank T2 or tank T3.

Whilst in the tanks T2 and T3, the water is recirculated through an ozone generator O2, using one of two recirculating pumps, respectively numbered P3a and P3b, until the ozone concentration reaches about 0.4 ppm.

Once an ozone concentration of about 0.4 ppm is reached, the now sterilised is
5 transferred from the tanks T2 and T3 to one of the tanks T4, T5 and T6.

When a desired amount of sterilised water has been transferred to one of the tanks T4,
10 T5 and T6, as may be determined by means of level measurements, a measured amount of precipitated magnesium carbonate powder is added to the sterilised water in the tank and mixed whilst the contents of the respective tank is being recirculated by means of one of three sets of circulating pumps P7A, P7B; P9A, P9B and P11A, P11B, one set being operatively connected to each of the tanks T4, T5 and T6. The two pumps of each set are used simultaneously to recirculate water of the respective tank, one of the pumps of these sets being operatively connected to a corresponding lower side entry nozzle located on the respective tank, whilst the other pump is operatively connected to a corresponding upper side entry nozzle located at a level about halfway up the side of the tank. The lower side entry nozzle is directed upwards, at an angle, whilst the upper side entry nozzle is directed downwards, at an angle. When the contents of the tank are circulated, the nozzles cause jets of water to be ejected into the contents of the tank, in a substantially vertical plane, rather than to swirl in a circular motion. It has been found that a circular motion is
15 disadvantageous in that it facilitates separation of the solids from the suspension rather than to facilitate mixing. The lower nozzle may be directed towards the centre of the reactor tank, at an angle to the vertical and the upper side entry nozzle may be directed downwards, towards the centre of the reactor tank, at an angle to the vertical. By mixing in the manner described, particularly if the conditions in the tank are sufficiently turbulent, an intimate contact between the magnesium carbonate particles and the water
20 can be achieved.

Whilst the contents of the respective tank T4, T5 or T6 is being mixed, a corresponding recirculating pump P6, P8 or P10 is used to contact the contents of the respective tank T4, T5 or T6 with carbon dioxide gas. The carbon dioxide gas is dissolved
30 in the water on the suction side of the respective pump P6, P8 and P10, by means of a carbon dioxide injector, before the carbonated water is returned to the respective tank T4, T5, T6.

The pH of the solution containing species resulting from the dissolution of carbon dioxide is monitored, and the dissolution of carbon dioxide is proceeded with until the pH is no lower than about 8.2. It has been found that if the pH is taken down too far, it takes a long time for it to return to the ideal range of about 8.2 to about 8.6.

Once a substantially clear solution of magnesium carbonate and magnesium bicarbonate has been produced in the tanks T4, T5 and T6, the contents is transferred to one of two bottling lines 1 and 2, by means of transfer and bottling pumps P12, P13.

Optional storage tanks T8, T9 are provided for storage of finished product.

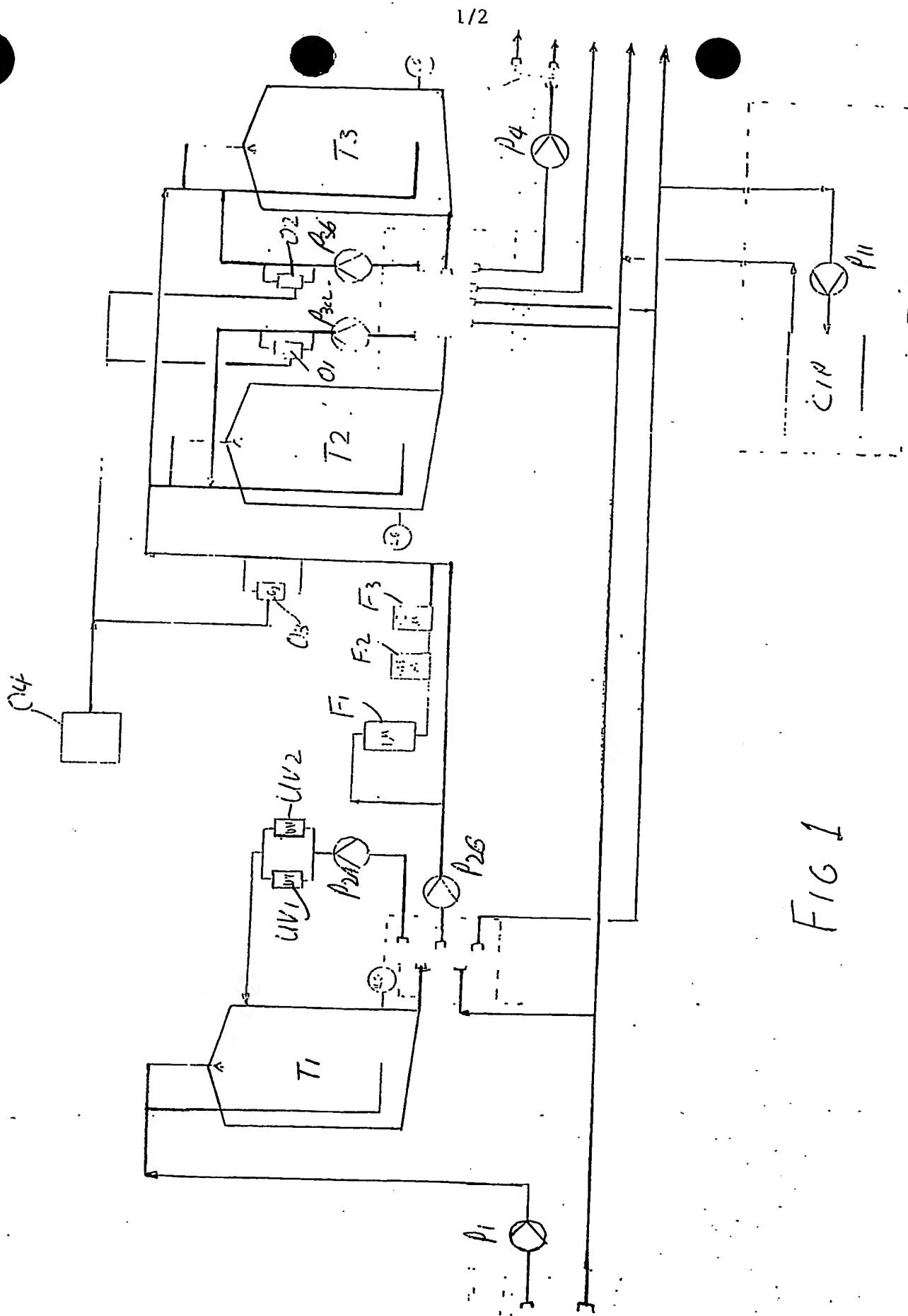
Conveniently, the apparatus 10 includes means (not shown) for controlling the pH of the solution.

The apparatus 10 may also include means (not shown) for controlling the pressure and/or the temperature of the solution.

The apparatus 10 may further include means (not shown) for bottling the said aqueous solution of magnesium bicarbonate.

15

Dated 19 August, 2002
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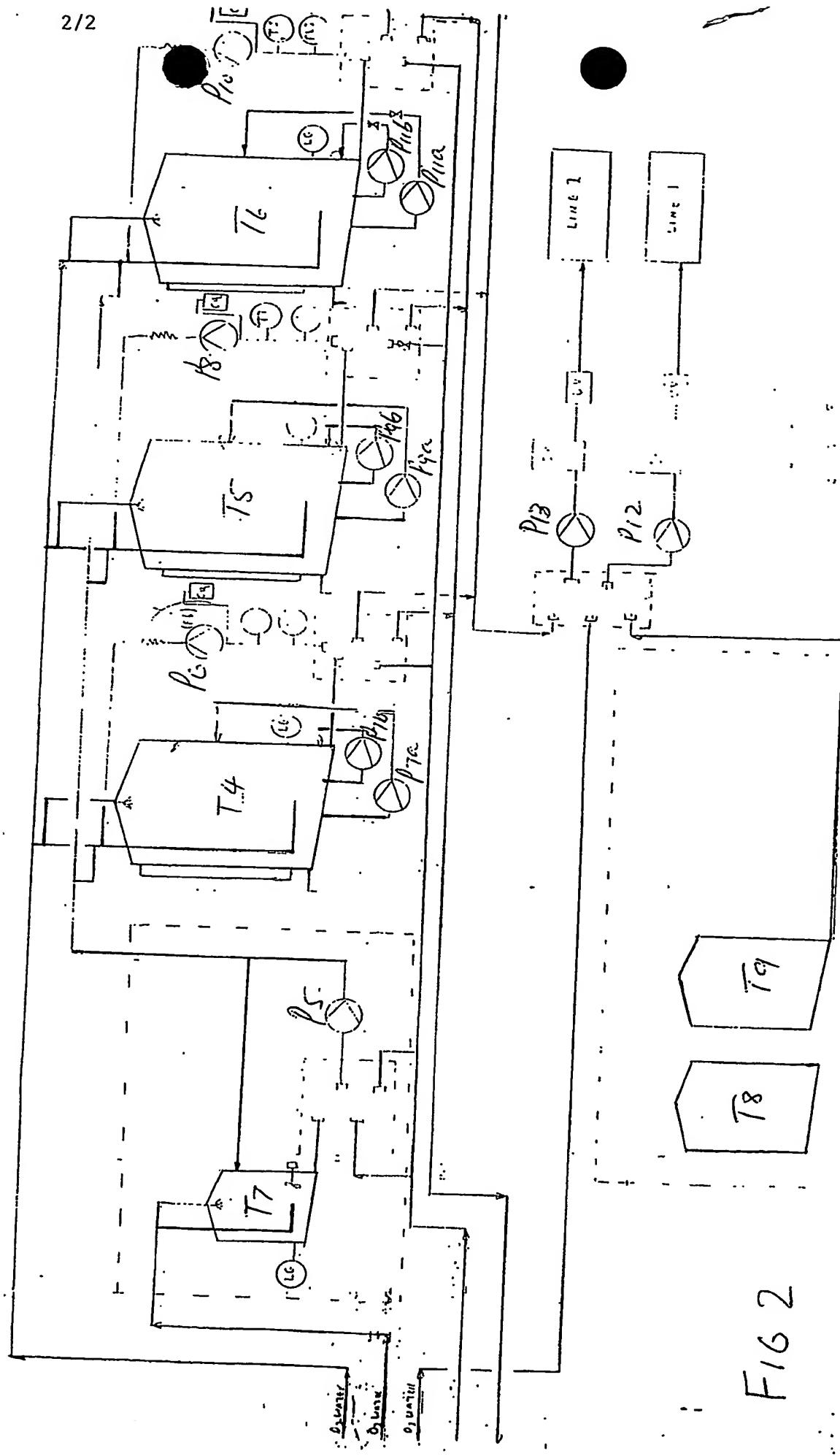


Fig 2